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# Wide band laser emission using solvated species of esculin

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**Abstract.** Coumarin derivatives are some of the most efficient dye laser systems in the blue green region of the spectrum. Some of the dyes belonging to this family exhibit a wide band of laser emission when placed in a suitable environment. This is possible in these dyes because the dye molecule can exist in different solvated forms, with each solvated form emitting laser light independently.

This paper pertains to a study of laser emission from 7-hydroxy-6-glucosido coumarin (otherwise known as Esculin) in its different solvated forms.

The dye was studied in various solvents such as alcohols, glycols, etc., and the different solvated forms of Esculin were produced in them by suitable addition of acid and base. The dye solution was excited by a Nitrogen laser and the super-radiant dye laser emission was monitored and the bandwidth of the emission determined.

By proper choice of the concentration of the ions one can have a very wide band laser emission from the dye solution, which is much wider than from any single solvated species. The details of this simple and elegant method of enhancing the bandwidth are presented in this paper.

## 1. Introduction

The hydroxy coumarins are generally very good media for high power broad band dye laser amplifiers. These dyes have large gain and under certain conditions, a laser emission bandwidth as large as 100 nm is possible. The hydroxy coumarins can exist in various solvated forms, in acidic or basic environment and these solvated species of the dye molecule absorb, fluoresce and work as lasers independently but simultaneously. The wavelength overlap of the laser bands of these solvated species are such as to give rise to a very wide laser emission band. Esculin is one of the coumarin dyes which has been investigated

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by us and the present study is the first to report on the wide band laser emission characteristics of this dye.

## 2. Experimental

Esculin was obtained from Hopkins and Williams Ltd., Essex, London. The absorption and fluorescence spectra were recorded using dilute solutions of Esculin ( $5\times10^{-6}$) in isopropanol (analar grade). To produce a basic environment 10 percent of 0·089 *N* NaOH and to produce an acid environment 30 percent of concentrated HCl (2·5 *N*) was added to isopropanolic solutions of Esculin. The absorption spectra were recorded on a Carl-Zeiss DMR 21 spectrophotometer. The fluorescence spectra were obtained on an Aminco-Bowman spectrofluorometer.

The dye solutions of $5\times10^{-3}M$ concentration were transversely excited with a $N_2$ laser built by us and the superradiant laser output from the dye solutions was monitored with a prism monochromator and detected with an RCA 931 A photomultiplier tube and 141 A Hewlett Packard oscilloscope. The intensity of the dye laser as a function of wavelength was delineated for a fixed $N_2$ laser power. All the spectral intensities were then normalised.

Of the many groups of solvents tried such as esters, amides etc., Esculin has the widest laser bandwidth in alcohols and glycols to which a few percent of acid and base had been added.

## 3. Results and Discussion

### I. *Spectra of the different solvated species of Esculin*

The molecular structure of Esculin (7 hydroxy-6 glucosido coumarin) is given in figure 1. The absorption and fluorescence spectra of Esculin in neutral, basic and acidic isopropanol are given in figure 2. The laser spectra of these species are shown in figure 3.

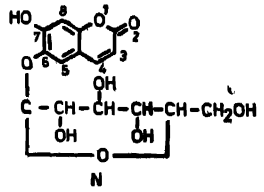


**Fig. 1.** Neutral form of Esculin

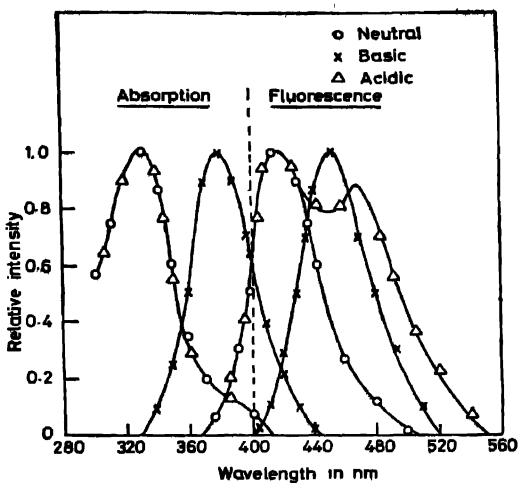


**Fig. 2.** Absorption and fluorescence spectra of esculin

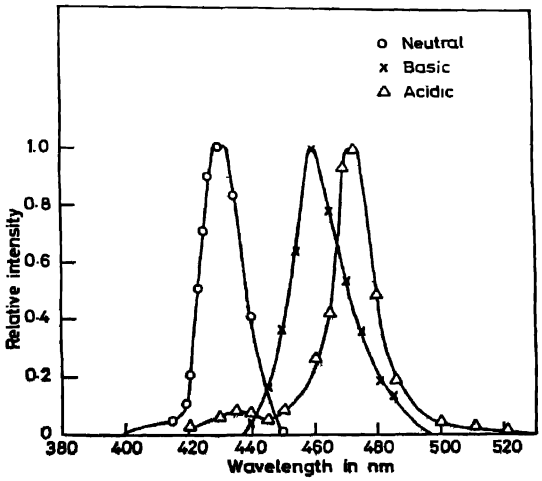


**Fig. 3.** aser emission spectra of esculin

(a) *In neutral alcohol*

Coumarin is a six membered oxygen-heterocyclic aromatic compound. It may be considered as a fusion of benzene and pyrone moities. The presence of oxygen in the first position and a carbonyl group in the second position makes the benzene part relatively acidic compared to the pyrone part, and enhances the mobility of the $\pi$ electron cloud and hence the resonance of the system. In general, for coumarin, an electron donating substituent such as a hydroxy group in the seventh position and an electron attracting substituent such as a cyano group in the third position enhance the resonance still further and produce stronger auxochromic effects. Hence these substituents help produce high intensities in absorption fluorescence and laser emission. Thus, Esculin with a hydroxy substitution in the seventh position is a good dye laser medium. The glucosido group in the sixth position has an insignificant effect in producing wavelength shifts of the spectra since it is insulated from the homocyclic part, and hence intramolecular charge transfer is inhibited. However, the glucosido group, because of its bulk, can twist the molecule out of planarity and result in a slight reduction of the absorption, emission and lasor intensities of the dye.

The chromophoric system of the dye extends from the carbonyl part in the second position to the hydroxyl part in the seventh position. In neutral alcohol, the absorption peak is around 335 nm, the fluorescence peak is around 420 nm and the laser peak is 430 nm. The peak of the laser emission is shifted by 10 nm towards the redside of the fluorescence peak.

(b) *In basic alcohol*

The phenolic side of the dye is acidic and the pyrone part of it is basic. In the ground state, the dye undergoes an acid—base reaction when NaOH is added to the solution, as shown in figure 4. The anion of the dye exists as an ion in the solution and has its absorption peak around 380 nm, its fluorescence peak around 455 nm, and its laser emission peak is around 460 nm.

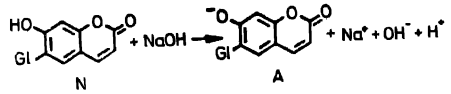


**Fig. 4.** N–Neutral form of esculin
A–Anionic form of esculin
G–Glucosido group

The absorption band around 380 nm which appears and grows in intensity with increasing concentration of NaOH is indicative of a ground state acid-base reaction, giving rise to the anionic form of Esculin. By carefully controlling the concentration of NaOH it is possible to have both the neutral and aninonic species of Esculin present simultaneously. Addition of large amounts of NaOH leads to complete ionisation of the neutral form leaving only the anionic form.

The intensity of fluorescence and laser emission is many times greater in basic ethanol than in neutral alcohol for the same concentration of the dye. This indicates that the anion has a higher quantum yield of fluorescence and a smaller excited state lifetime than the neutral species.

(c) *In acidic alcohol*

The absorption spectrum of the acidified alcoholic solution of Esculin remains identical with the neutral species, whatever be the amount of and the concentration of acid added to it. But its fluorescence spectrum differs from the fluorescence of the neutral species. A new band of fluorescence appears around 470 nm and this grows in intensity with increasing acid concentration.

Since the absorption spectrum of the acidic form is similar to that of the neutral form it suggests that dye undergoes acid-base reaction in the excited state only. This may be contrasted with the ground state reaction in a basic environment. This is probably because the pyrone part of the dye becomes adequately basic to accept a proton only in the excited state.

The acid form of Esculin may be described by the following reaction (see Figure 5). The dye exists as a tautomer in the excited state and has no stable ground state. It dissociates into neutral Esculin when it returns to the ground state. This behaviour is very similar to that observed for 4 Methyl umbelliferone (4 Mu) in acid environment by Dienes *et al* and Yakatan *et al*.

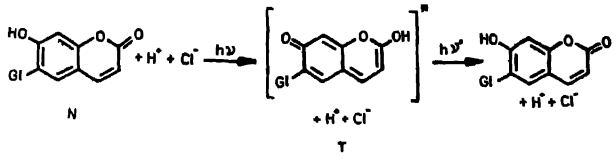


Fig. 5. N Neutral form of Esculin
T Tautomer of Esculin formed only in the excited state
Gl Glucosido group

The fluorescence and laser output exhibit a high intensity from the acidic form relative to that from the neutral form, but is lower than that from the anionic form. This indicates that the gain of the neutral species of Esculin is the lowest and the gain of the anionic form is the highest.

The fluorescence peak for acid form is around 470 nm and the laser peak for this form is red shifted with respect to the fluorescence and occurs around 475 nm.

II. *Wide band Laser Emission from Esculin*

By a suitable combination of alcohol, acid and base one can make all the three solvated forms of Esculin coexist. These three species absorb, fluoresce and produce laser emission independently and simultaneously. Figure 6 gives the laser spectra of the dye solution having all the solvated form present simultaneously. Curve 1 shows the laser emission spectra for Esculin in isopropanol with 15 percent of 2·5 *N* HCl. The laser emission band around 430 nm is due to the neutral species and that around 475 nm is due to the acidic forms. The dip or valley around 465 nm is due to the absence of the anionic species. Addition of 1% of ·089 *N* NaOH reduces this valley. Curve 2 shows the laser spectrum for such a combination of acid and base. Addition of larger amounts of NaOH to reduce this valley further, does not help, because large amounts of NaOH bring about complete ionisation. Further, there is considerable overlap of the absorption band of the anionic species and the laser emission band of neutral species.

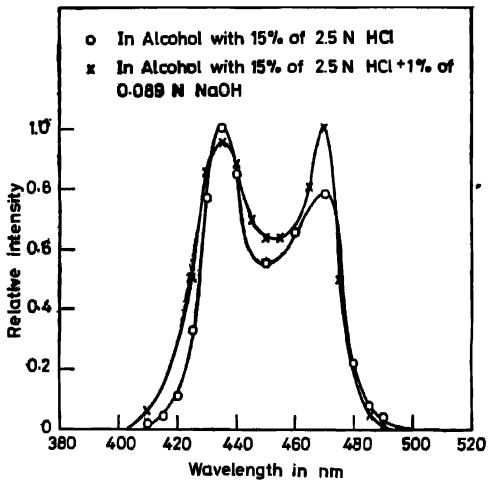


**Fig. 6** Wide band laser emission from Esculin

With the above combination of acid and base we were able to obtain a wide band laser emission of about 100 nm from Esculin. This width is considerably smaller than that of the wideband laser emission from 4 Methyl Umbelliferone investigated by others. This is due to the fact that for 4 Methyl Umbelliferone the wavelength separation of the various species is very much greater than that in Esculin.

**Acknowledgment**

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**References**

Dienes A, Shank C V and Kohn R L *IEEE Journal of Quantum Electronics QE* 9 No 8 pp 833
Yakatan G J, Juneau R J and Schulman S G *Analytical Chemistry* 44 00 1044